Electrodialysis with bipolar membrane for regeneration of a spent activated carbon

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ABSTRACT

The main purpose of the present work was to develop a treatment method to regenerate granular adsorbent beds saturated with H_2S by utilizing three electrodialysis compartments equipped with a cation or an anion exchange membrane or a bipolar membrane. Three electrodialysis compartments were utilized under various experimental parameters to determine the optimum conditions for the recovery of column particles saturated by H_2S. The desulphurization operation is achieved with the extent of extraction close to 90% and an electric current density of about 30%.

Use of the bipolar membrane makes it possible to regenerate the saturated adsorbent granules without adding chemical products. Since the only reagent was electricity, the projected economics are very attractive.

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1. Introduction

The control of hydrogen sulphide emissions has significantly increased following the increase of environmental concern and stricter regulations. Activated carbon is predominantly an amorphous solid adsorbent most widely used as adsorbents of gases and vapors. This is due to their large specific surface area exceeding $1000\,m^3/g$, high pore volume, high density of carbon atoms in graphite-like layers, and surface hydrophobicity, combined with their catalytic influence on numerous chemical reactions and unique surface chemistry [1,2].

Activated carbon adsorbs molecules from both liquid and gaseous phases depending upon the pore size distribution of the adsorbent [3].

One of the environmental applications of activated carbons is the removal of hydrogen sulphide odor from effluent air in wastewater treatment plants [4–7].

Catalytic oxidation of H_2S occurs on the surface of activated carbon, hydrogen sulphide is oxidized either to sulphur or sulphur dioxide which cause a gradual decrease in the capacity leading to exhaustion of the carbon as adsorbents. The spent activated carbon previously used as hydrogen sulphide adsorbent has to be replaced by a fresh or regenerated material. In the last decade, the option for regeneration of activated carbon by using water has appeared [8–11].

The goal of this study was, therefore, to develop a process using a combination of electrodialysis equipped with a bipolar membrane and an adsorption column. Three electrodialysis compartments were utilized under various experimental parameters to determine the optimum conditions of recovery of column particles saturated by H_2S.

To determine the performance of the electrodialysis process the extent of extraction and the current efficiency were calculated.

The extent of extraction is expressed by the following ratio:

$$R_{ext} = \left(1 - \left[\frac{n_{S^{2-}}^t \text{ (dilute)}}{n_{S^{2-}}^0 \text{ (dilute)}}\right]\right) \times 100 \qquad (1)$$

where $n_{S^{2-}}^t$ and $n_{S^{2-}}^0$ are the mole numbers of S^{2-} ions in the dilute compartment at times t and 0, respectively.

The current efficiency may be calculated by the equation:

$$R_F = Z_{S^{2-}} \times n_{S^{2-}}^t \times \frac{F}{i} \times t \qquad (2)$$

where $Z_{S^{2-}}$, $n_{S^{2-}}^t$, F, and i are, respectively, the electrochemical valence of the sulphur ion, the mole number of the sulphur ion in the dilute compartment at time t, the Faraday constant and the current density.

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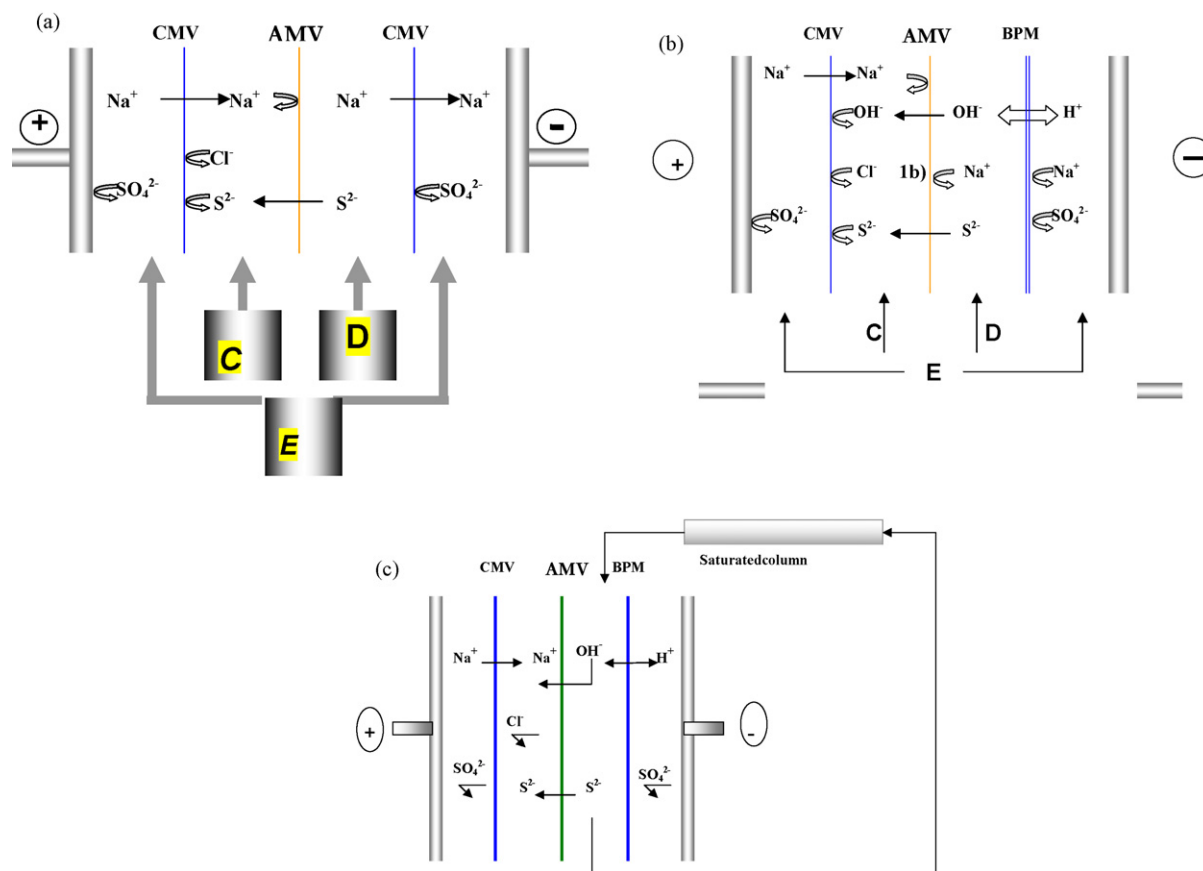
Fig. 1. The electrodialysis cell. (a) Equipped with ions exchange membrane. (b) Equipped with a bipolar membrane. (c) Three electrodialysis compartments combined with packed column. D: dilute compartment (sulphur solution); C: concentrate compartment; e: electrodes compartment; AMV: anion exchange membrane, CMV: cation exchange membrane; and BPM: bipolar membrane.

Table 1
Characteristics of membranes.

Code	Manufacturer	Brand	Standard	R ($\Omega\,cm^{-2}$)	C_E (mequiv./g)	e (μm)
AMV	Asahi Glass	Sélémion	AEM	2	1.2	110–150
CMV	Asahi Glass	Sélémion	CEM	2.7	2.4	110–150
MBP	Tokoyama soda		BPM			

2. Materials and methods

The electrodialysis apparatus consisted of four circulating batch systems and cells. Each batch system was composed of a holding tank and a circulation pump. The electrodialysis cell, presented in Fig. 1, was composed of 4 compartments divided either with a cation exchange membrane (Selemion CMV-Asahi Glass) (Fig. 1a), and an anion exchange membrane (Selemion AMV-Asahi Glass) or a bipolar membrane (Neosepta BPM-Tokuyama Soda) (Fig. 1b). The effective membrane area was $50\,cm^2$. The characteristics of membranes are shown in Table 1. Each platinum-coated titanium plate electrode had the same surface area as the membrane. The central compartment was used as a dilution compartment where the S^{2-} and Na^+ ions were transported across ion exchange membranes while the hydroxyl ions were produced by the bipolar membrane in this compartment.

A technique developed by Lounici et al. [12] was used for activation of granular activated carbon (GAC).

It was based on the electrochemical method. The electro-activation time is about 30 min and the optimum potential ranged from +200 mV/SCE to +400 mV/SCE. The limiting adsorption capacity was improved by about 55% at the applied electrochemical potential $E = +300$ mV/SCE. The main characteristics of the GAC are presented in Table 2.

The main purpose of the bipolar membrane was to produce the hydroxyl ions which made possible the regeneration of the saturated column by ion exchange (between these ions and the sulphur ions adsorbed onto granules in the column).

During electrodialysis experiments, the voltage across the stack, current density, pH, volumes and composition of the tanks were measured as a function of time. All experiments were performed at room temperature ($20 \pm 4\,^\circ C$).

Table 2
Chemical and physical characteristics of the granular electro-activated carbon.

Carbon	Parameter average value
Total ash (%)	3.59
Moisture (%)	9.6
Porosity	0.4
Density (g cm^{-3})	1.54
Iodine ASTM (mg g^{-1})	952.5
pH at 20 °C	5.7
Specific surface area-BET (m^2 g^{-1})	1045

The sulphur concentrations were determined by potentiometry using the specific electrode Ag/S^{2-} (EA306-Metrohm). The sodium ion concentrations were titrated by flame photometry using a Spectra 620 ABQ photometer.

The sulphur adsorbent was prepared by using granular activated carbon having particle size of about 2 mm. The granular was then packed in a column and submitted to H$_2$S gas until saturation. The H$_2$S gas was generated by an equimolar reaction of ZnS and H$_2$SO$_4$ solution. The H$_2$S gas was passed through a column of granular activated carbon by the mean of vacuum pump.

Regeneration of GAC packed in bed saturated with H$_2$S was realized by integrating the column into the dilute circuit (Fig. 1c) which provided hydroxyl ions via the bipolar membrane, and thus desulphurized the GAC by ion exchange between the sulphur compounds adsorbed onto the granules and the OH$^-$ ions.

3. Results and discussion

3.1. Efficiency of electrodialysis in extracting the sulphur compound ions

Before combining the adsorption column and the electrodialysis apparatus, it was important to test the efficiency of electrodialysis for concentrating the sulphur ions in the concentrate compartment. In this case, it is important to assess the competition between hydroxyl ions and sulphur ions and to determine the optimum experimental conditions for the process.

The electrodialysis apparatus was tested by using sulphur salt. The current density ranged from 5 to 30 A m^{-2}. A higher voltage

did not allow an increase in current density without damage the electrodialysis membranes. Indeed, the polarization curve giving the potential (E) against the current density (i) (results not shown) indicates that the process operated in faradic zone (linear relationship between E and i) with i not exceeding 35 A m^{-2}. The water dissociation occurred, that involve formation of hydroxides which may damage exchange anion membranes.

The desulphurization operation was achieved with three-compartment electrodialysis equipped with the CMV or BPM membranes (Fig. 2). Desulphurization of the dilute compartment (Fig. 2a and b) was realized. It was observed that the current density i = 30 A m^{-2} reduced the sulphur ions concentration most rapidly. On the other hand, in the concentrate compartment, the concentration of sulphur ions increased more rapidly at i = 30 A m^{-2} than at other current densities (Fig. 2c and d). It is clear that a current density of about i = 30 A m^{-2} gave the best performance for the desulphurization operation with three-compartment electrodialysis equipped with the CMV or BPM membranes. This highest current density value made it possible to minimize the effect of the competition between the hydroxyl ions (provided by the bipolar membrane) and the sulphur ions. It is well known that when the [OH$^-$] concentration becomes too high (i.e., at high current densities, since the production of H$_3$O$^+$ and OH$^-$ depends on the intensity of the current), there is competition between the electro-transport of OH$^-$ and S^{2-}. It is clear in this case that the electrical conduction was achieved by the transport of the high-mobility hydroxyl ions [13]. It is also important to consider the H$_3$O$^+$ ions provided by the bipolar membrane (BPM). Indeed, the sodium concentration in the dilute compartment was practically constant (Fig. 3). On the other hand, an increase and a
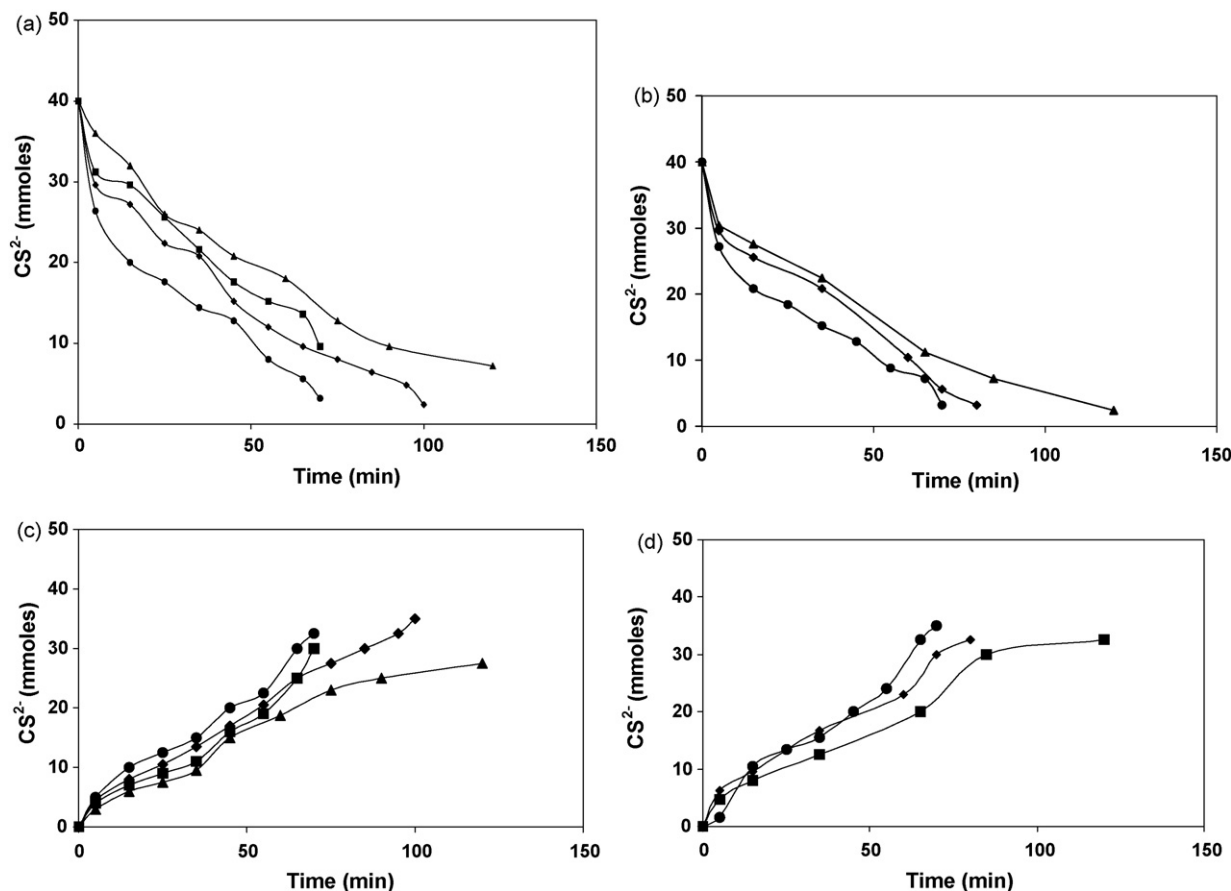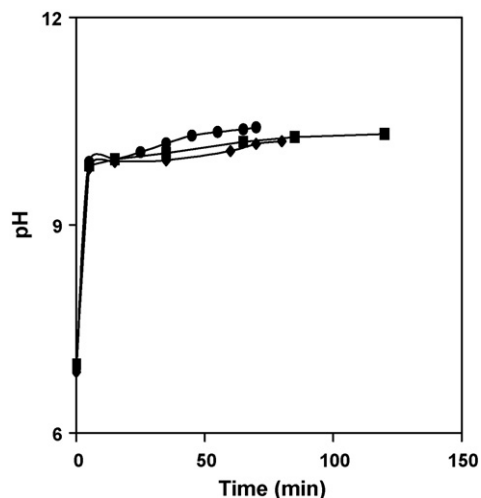

Fig. 2. Variation of the sulphur concentration (CS^{-2}) during the desulphurization operation at various current density: (*r*) 30 A m^{-2}, (♦) 20 A m^{-2}, (❷) 10 A m^{-2} and (i) 5 A m^{-2}. (a) In dilute compartment with the CMV membrane. (b) In concentrate compartment with the CMV membrane. (c) In dilute compartment with the BPM membrane. (d) In concentrate compartment with the BPM membrane.
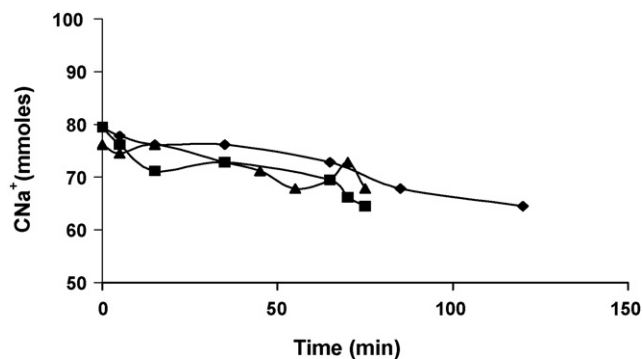
Fig. 3. Variation of the sodium concentration (CNa^+) during the desulphurization operation at various current density: (r) 30 A m^{-2}, ($\blacklozenge$) 20 A m^{-2}, (❷) 10 A m^{-2} and (i) 5 A m^{-2}.

Fig. 4. Variation of pH during the desulphurization operation in concentrate compartment with electrodialysis equipped with BPM.

decrease were determined, respectively, in the concentrate and electrolyte compartments (results not shown), which indicates that at high current density a competition between Na$^+$ and H$_3$O$^+$ ions (provided by BPM) was encountered in the electrolyte compartment. Indeed, Na$^+$ ions contribute more to assuring the transport through the CMV membrane at $i = 10$ A m^{-2} and $i = 20$ A m^{-2} than at $i = 30$ A m^{-2}; at the higher current density, the excessive production of H$_3$O$^+$ makes the competition possible. Because of their higher mobility compared with that of Na$^+$, H$_3$O$^+$ ions cross the cation exchange membrane more easily and then produce a neutralization reaction with OH$^-$ in the concentration compartment (Fig. 4).

The current efficiency and the extent of extraction, which are important parameters, were determined. The results, presented in Fig. 5a, confirm that at $i = 30$ A m^{-2} a high extent of extraction (about 90%) was obtained with an experimental time not exceeding 20 min; however, it required 35 min and 60 min with $i = 20$ A m^{-2} and $i = 10$ A m^{-2}, respectively.

The results, presented in Fig. 5b, confirm that for high current density the amount of OH$^-$ generated is too high; consequently, the
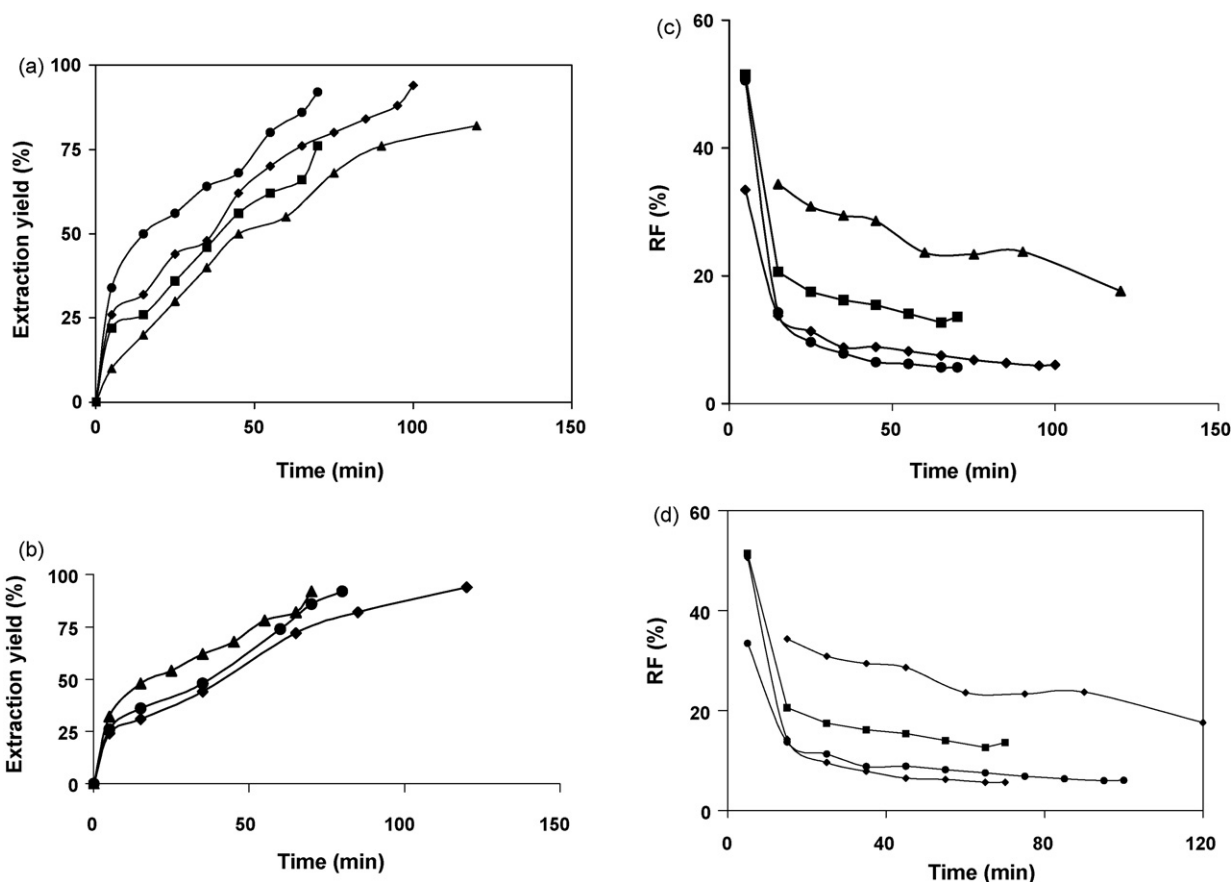
Fig. 5. Variation of an extent of extraction and current efficiency during the experiments in dilute compartment: (r) 30 A m^{-2}, ($\blacklozenge$) 20 A m^{-2}, (❷) 10 A m^{-2} and (i) 5 A m^{-2}. (a) Extraction yield change in dilute compartment with the CMV membrane. (b) Extraction yield change in dilute compartment with the BPM membrane. (c) Current efficiency (RF) change in dilute compartment with the CMV membrane. (d) Current efficiency (RF) change in dilute compartment with the BPM membrane.
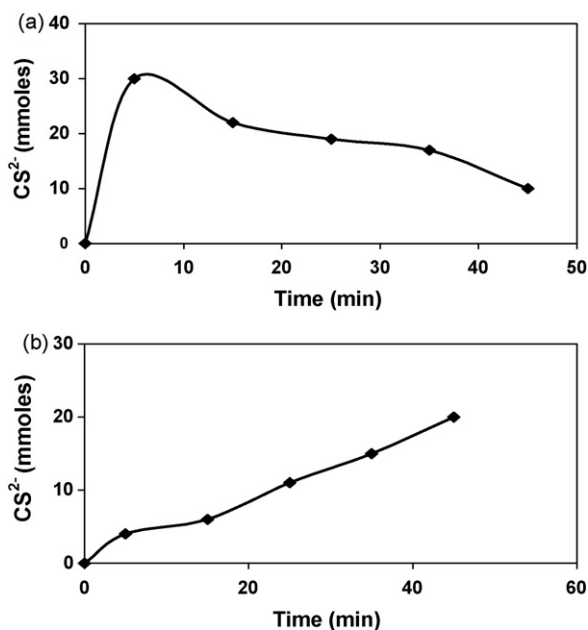
Fig. 6. Change of the sulphur concentration (CS^{2-}) in dilute (Fig. 5a) and concentrate (Fig. 5b) compartment with the complete desulphurization process at optimum experimental condition. $i = 20\,A\,m^{-2}$.

Fig. 7. Variation of the pH in dilute compartment during the desulphurization of saturated GAC column by combination with electrodialysis equipped with BPM membrane.
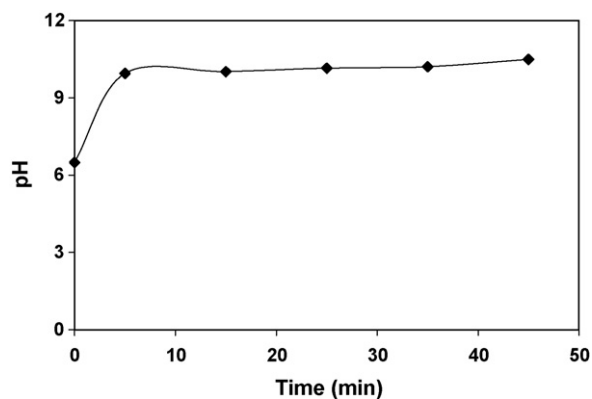
electric current is partly carried by the hydroxyl ions, and the R_F is low.

It was found that electrodialysis using three compartments with two exchange membranes and a bipolar membrane made possible the extraction of sulphur compounds with an acceptable extent of extraction and current efficiency. The desulphurization operation is achieved with the extent of extraction close to 90% and an electric current density of about 30%.

In reality, the kinetics of the desorption of the sulphur compounds have to be considered, since these ions will be desorbed by ion exchange between these compounds adsorbed on GAC composing the column and the hydroxyl ions provided by BPM membranes. It is clear that the efficiency of the process has to be tested on the complete process, i.e., electrodialysis integrated with the saturated column or linked with the dilute compartment.

3.2. Study of the electrodialysis–saturated GAC column combination

The performance of the desulphurization process combining the H_2S saturated GAC column and the electrodialysis apparatus was studied at an optimum current density of $i = 30\,A\,m^{-2}$, previously determined (Fig. 6). The results obtained show that desorbed sulphur ions were obtained by ion exchange between chloride and sulphur ions before the utilization of the electrodialysis. These sulphur concentrations ranged, moreover, from 0.2 to 0.4 mol/l. Electrodialysis makes it possible to reduce considerably the concentration of the sulphur ions in the dilute compartment and at the same time increase the concentration of this species in the concentrate compartment. It was, however, observed that the reduction of the sulphur ions concentration was fast during the first 15 min and that it then reached a limiting value. These results may be explained by the fact that in the first 15 min, the amount of the sulphur ions released instantaneously was electrotransported through the anion exchange membrane, and after this an equilibrium was established between the three phenomena: the ion exchange phenomenon between OH^- and sulphur ions, the production of OH^- by the bipolar membrane and the electro-

transport of the desorbed sulphur ions through the anion exchange membrane.

Determination of the evolution of the pH in the dilute compartment (Fig. 7) during the desulphurization operation confirmed that the hydroxyl ions were not totally consumed by ion exchange with the sulphur-adsorbed ions; an increase of the pH was then observed.

Increasing of the pH in the dilute compartment results from the production of hydroxyl ions resulting from water dissociation mechanisms taking place in the bipolar membrane and the releasing of S^{2-} is due to crossing of dilute solution through the saturated column can be achieved without requiring any addition of chemicals.

4. Conclusion

The desulphurization operation by electrodialysis technique equipped with bipolar membrane is achieved with the extent of extraction close to 90% and an electric current density of about 30%.

The combined electrodialysis/column process removed sulphur compounds adsorbed onto GAC. Use of the bipolar membrane makes it possible to regenerate the saturated adsorbent granules without adding chemical products. Since the only reagent was electricity, the projected economics are very attractive.

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